

Fragmentation Processes Following Core Excitation in Acetylene and Ethylene by Partial-Ion-Yield Spectroscopy

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INTRODUCTION

When a core hole is induced in a molecule, either below or above a core ionization threshold, dissociation is likely to occur following or even during electronic relaxation. The main pathway to fragmentation is the decay of the species with a core hole to molecular ions with a single positive charge (mainly below threshold) or a double positive charge (mainly above threshold) which are metastable and subsequently dissociate by breaking one or more chemical bonds. The observation of the charged species (molecular ions or fragment ions) is very informative of the nature of the excited or ionized state and of the dynamics of the photofragmentation process. Such experiments are performed with synchrotron radiation by monitoring the ion yield of all ion fragments (total-yield mode) or of individual ion channels (partial-yield mode) as a function of photon energy in the range including a core ionization threshold. In the present work we investigated the ion-yield spectra of two simple representative hydrocarbons, acetylene and ethylene, in the photon energy region including the C 1s ionization threshold.

EXPERIMENTAL

Our measurements were performed on undulator beamline 8.0.2, at the Advanced Light Source, Lawrence Berkeley National Laboratory. The monochromator resolution at 300 eV was approximately 70 meV using an entrance-slit width of 15 microns and an exit-slit width of 20 microns. This resolution was chosen to allow a reasonable signal while still being able to observe the higher Rydberg states near the carbon *K* edge. The experimental apparatus used in the present study has been described previously [5]. Basically, the apparatus consists of an 180° magnetic mass spectrometer (resolution of one mass in 50), and a lens system to focus the ions created in the interaction region onto the entrance slit of the mass spectrometer, and an open gas cell which contains both a push plate and an extraction plate to move the ions created in the interaction region into the lens system. The target gas enters the open cell via an effusive jet two mm in diameter. A Dr. Sjut's channel electron multiplier is used at the exit slit of the magnetic spectrometer to detect the ions. Finally, a differential-pumping system was used to isolate the target-chamber vacuum (2×10^{-5} torr) from the beamline vacuum (1×10^{-9} torr).

RESULTS AND DISCUSSION

Absorption spectra for acetylene and ethylene by total-electron or total-ion yield (including symmetry-resolved) have been obtained by several groups with an instrumental resolution better than the core-hole-lifetime broadening [1-4]. Vibrational fine structure and vibronic coupling have thus been observed already. However, the experimental methods used have been limited to the simultaneous observation of all channels in either electron emission or ion emission. We have obtained for the first time single-channel measurements, *i.e.*, partial-ion yields for all detectable fragments as a function of photon energy around the C 1s threshold in both systems. The relative strength of the various channels and the intensity distribution within each of them are mostly informative on the fragmentation dynamics of both species. In particular, below threshold we observe that the relative intensity for the spectral features related to core-to-

Rydberg excitation increases as the fragmentation process is more extended (*i.e.*, for the smaller fragments the Rydberg states are much more prominent than for the parent molecular ions). This is directly related to the fact that spectator decay is much more probable following excitation to diffuse Rydberg orbitals, and many or most of the final two-hole/one-particle states are dissociative. This experimental finding sheds new light on the level assignment in acetylene, where it is possible now to discriminate between states mainly with σ^* or Rydberg character.

REFERENCES

1. Y.Ma, C.T.Chen, G.Meigs, K.Randall and F.Sette, Phys.Rev.A **44**, 1848 (1991)
2. F.X.Gadea, H.Köppel, J.Schirmer, L.S.Cederbaum, K.J.Randall, A.M.Bradshaw, Y.Ma, F.Sette and C.T.Chen, Phys.Rev.Lett. **66**, 883 (1991)
3. B.Kempgens, B.S.Itchkawitz, J.Feldhaus, A.M.Bradshaw, H.Köppel, M.Döscher, F.X.Gadea and L.S.Cederbaum, Chem.Phys.Lett. **277**, 436 (1997)
4. J.Adachi, N.Kosugi, E.Shigemasa and A.Yagishita, Chem.Phys.Lett. **309**, 427 (1999)
5. W. C. Stolte et al., J. Phys. B **30**, 4489 (1997).

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